SCANNING PROBE MICROSCOPY AND SPECTROSCOPY

Methods and applications

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Introduction

The general principle of operation of a scanning tunneling microscope (STM) – and related scanning probe microscopies (SPM) as well – is surprisingly simple. In STM a bias voltage is applied between a sharp metal tip and a conducting sample to be investigated (metal or doped semiconductor). After bringing tip and sample surface within a separation of only a few Ångström units[1] (1 Ångström unit (Å) = 0.1 nanometer (nm) = 10^{-10} m), a tunneling current can flow due to the quantum mechanical tunneling effect before 'mechanical point contact'[2] between tip and sample is reached. The tunneling current can be used to probe physical properties locally at the sample surface as well as to control the separation between tip and sample surface. The distance control based on tunneling is very sensitive to small changes in separation between the two electrodes because the tunneling current is strongly (exponentially) dependent on this separation, as we will see later (section 1.2). By scanning the tip over the sample surface while keeping the tunneling current constant by means of a feedback loop, we can follow the surface contours with the tip which – to a first approximation – will remain at constant distance from the sample surface. By monitoring the vertical position z of the tip as a function of the lateral position (x, y), we can get a three-dimensional image $z(x,y)$ of the sample surface. Motion of the tip both laterally and vertically with respect to the sample surface can be realized with sub-atomic accuracy by means of piezoelectric drives. The historical schematic drawing of the STM set-up is shown in Fig. 0.1.

The STM can be viewed as a powerful combination of three important conceptions: scanning, vacuum tunneling and point probing. Scanning

[1] The Ångström unit (Å) will often be used rather than the nanometer because it is the most appropriate length unit for dealing with structures on an atomic scale.

[2] The onset of mechanical point contact may not yet be clear conceptually. Possible definitions are provided later (section 1.21).

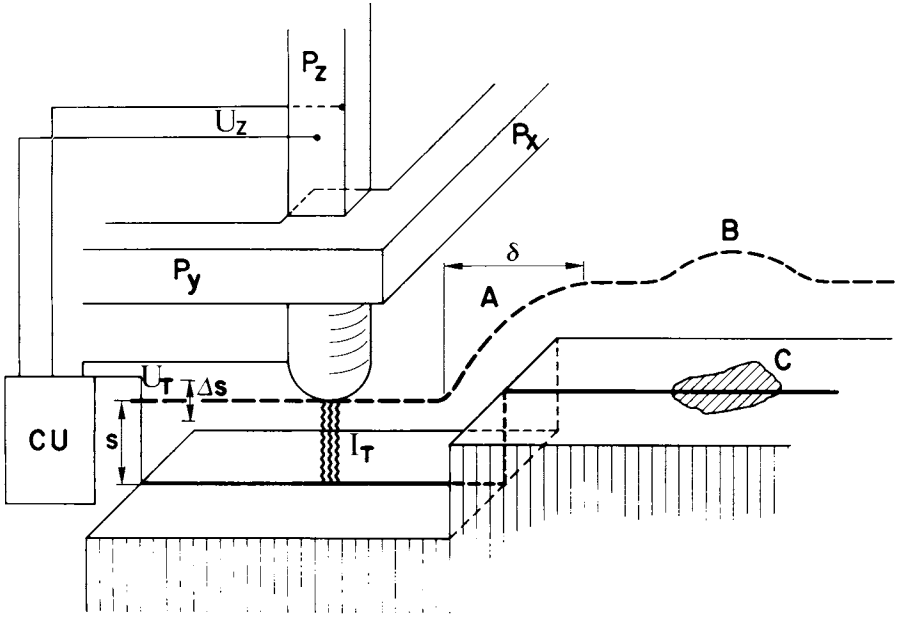

Fig. 0.1. Principle of operation of the STM. (Schematic: distances and sizes are not to scale.) Piezodrives P_x and P_y scan the metal tip over the surface. The control unit (CU) applies the appropriate voltage U_z to the piezodrive P_z for constant tunnel current I_T at constant tunnel voltage U_T. The broken line indicates the z displacement in a scan over a surface step (A) and a chemical inhomogeneity (B) (Binnig *et al.*, 1982b).

as a means for image generation is well known from other microscopies, e.g. scanning electron microscopy, or from television. Electron tunneling had already been used as a powerful experimental technique to probe physical properties of materials a long time before the invention of the STM. However, the tunnel junctions had a planar geometry and an oxide was used to separate the two planar metal electrodes. The tunnel barrier in these metal–oxide–metal tunnel junctions was neither adjustable nor well defined, due to inhomogeneities in the thickness of the oxide layer. Nevertheless, electron tunneling had already proved very important, particularly for probing the superconducting state (section 1.3). The STM makes use of a local geometry which is offered by a point probe tip as one of the two metal electrodes. Point probes have also been used successfully in the past, e.g. in point contact spectroscopy (section 1.7).

In summary, the scanned point-like tip probing the sample locally via vacuum tunneling of electrons makes STM a unique microscopy. It

needs no lenses, unlike other electron microscopes; therefore image distortions due to aberration cannot occur. The electrons involved in STM have an energy of no more than a few electronvolts (eV), in contrast to high-resolution electron microscopes where the electrons have energies of several keV up to MeV, making radiation-induced sample changes and damage very likely. In STM, the electron energies are even smaller than typical energies of chemical bonds, allowing non-destructive atomic resolution imaging. It may be argued that an electron energy E of about 1 eV, as is typical for STM experiments, may not be high enough to resolve individual atoms because the corresponding electron wavelength

$$\lambda = 12.25 \text{ Å} / \sqrt{E} \simeq 12 \text{ Å} \tag{0.1}$$

is larger than typical interatomic distances in solids of about 3 Å, which one would like to resolve. However, the STM is operated in the so-called 'near-field' regime where the distance d between tip and sample surface of typically a few Ångström units is comparable to or less than the electron wavelength λ: $d \lesssim \lambda$. In this regime, the spatial resolution which can be achieved is no longer diffraction-limited and is not determined by λ (chapter 3).

In contrast to other electron microscopes and surface analytical techniques using electrons, STM can be operated in air and in liquids as well as in vacuum because there are no free electrons involved in the STM experiment. Therefore, the application of STM is not limited to surface science, but has particularly great potential for *in situ* electrochemical studies and *in vivo* investigations of biological specimens. STM investigations of the important solid–liquid interface may have even greater impact in the future than STM studies of the solid–vacuum interface because only a very limited number of *in situ* analytical techniques for the solid–liquid interface are available. However, the most significant experimental results during the first ten years of STM have been obtained under ultra-high vacuum (UHV) conditions on well-defined sample surfaces. Here, STM has profited a lot from the knowledge and experience which had been accumulated in the past decades by surface scientists regarding sample surface preparation and UHV technology.

The most important feature of STM, however, might be that this type of microscopy provides local information, ultimately with atomic resolution, directly in real-space, in contrast to diffraction experiments which are traditionally used for determination of the structure of condensed matter. Real-space information is particularly important for the

study of non-periodic features such as defects (vacancies, interstitials, impurity sites, steps, dislocations and grain boundaries) and other chemical inhomogeneities. Therefore, STM has the greatest potential for the investigation of complex systems such as multicomponent materials, polycrystalline samples with grains and grain boundaries, composites and nanostructured materials. Other spatial inhomogeneities, e.g. flux vortices in type II superconductors or domain walls in magnetic materials, can also be probed by STM and related SPM techniques. The information gained by local probes, such as STM, and diffraction experiments can be regarded as complementary. Diffraction experiments provide information averaged over macroscopic sample volumes or surface areas and yield mean interatomic distances or lattice constants for crystalline materials with an accuracy which can never be reached by local probes. However, diffraction experiments generally do not provide an accurate picture of the degree of disorder and the nature of defect structures. For instance, it has become clear that a surface showing clear and sharp diffraction spots in low-energy electron diffraction (LEED) experiments can still appear highly defective when imaged by STM. On the other hand, the surface area which one is looking at by STM has been typically quite small (about 1 μm^2 or even less) in early STM investigations. This 'tunnel vision' might sometimes be dangerous when drawing conclusions for the whole surface from information gained at only a few locations of small lateral dimensions. The problem of how representative the obtained STM results are, is at least partly solved by considerably increasing the total scan range of STM/SPM instruments.

The brightest prospects for STM/SPM are offered in the field of nanometer-scale science and technology. As electronic devices become increasingly smaller, there is a strong need for understanding the physical properties of matter on a nanometer scale. Technology at the nanometer level requires nanopositioning and control, nanoprecision machining and reproducible creation of nanometer-scale structures as well as the use and control of super-smooth surfaces. These are tremendous challenges for which STM/SPM can provide appropriate solutions as will be discussed in chapter 8.

The development of STM/SPM has had, however, even greater impact than would appear by considering only those aspects mentioned so far. It should be emphasized that STM/SPM has particularly stimulated interdisciplinary research, mainly for two reasons. Firstly, STM/SPM has found broad applications in many different scientific disciplines such as condensed matter physics, chemistry, biology, metrology and materials science. It is not only the use of the same type of

microscope which provides a joining link between a large number of scientists from different disciplines but also the existence of many common projects of interdisciplinary nature for which the application of the STM/SPM technique plays an important role. Secondly, as solid state scientists can now probe matter locally down to the atomic level, an increasing number of common scientific questions exist for scientists having backgrounds in atomic and molecular physics and chemistry who are starting from individual atoms and molecules and trying to understand more complex macromolecules (Fig. 0.2).

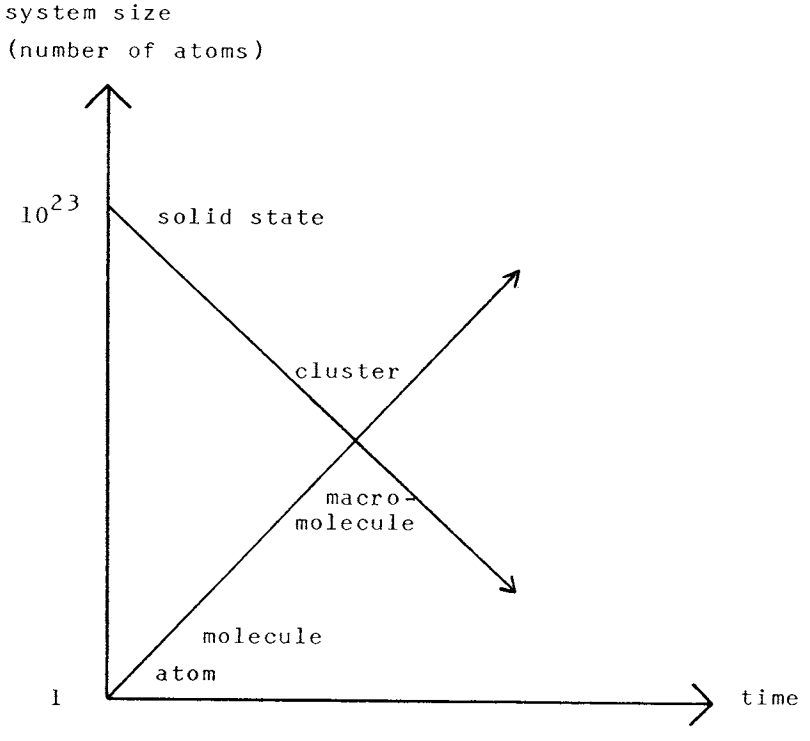

Fig. 0.2. Solid state physics deals with systems containing a large number (typically of order 10^{23}) of atoms. Traditionally, the collective physical properties of the whole ensemble of atoms have been studied by using macroscopic measurement techniques. Scanning probe methods now allow probing of physical properties of the solid state down to the scale of individual atoms. On the other hand, atomic and molecular physics aim at the understanding of the properties of larger molecules (macromolecules) based on the already known properties of single free atoms and smaller molecules. The time has now come at which an intersection of these two developments in research leads to an increasing common interest within these two originally different branches in physics and chemistry.

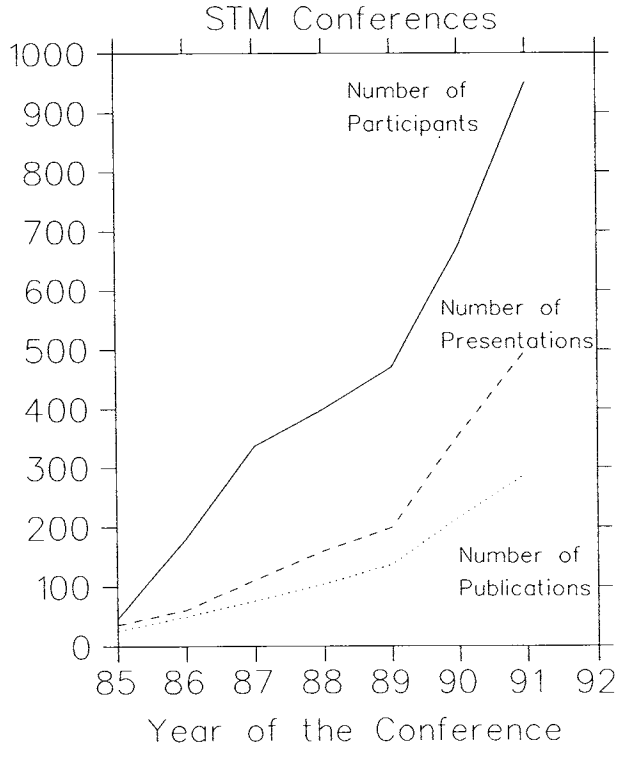

Fig. 0.3. Statistics of STM conferences between 1985 and 1991. Plotted are the number of participants, the number of presentations and the number of publications in the STM conference proceedings.

Furthermore, STM/SPM-type instruments are particularly attractive for universities, where education and research are equally important. Careful design and fine machining of the mechanical parts of the instruments are as important as a profound background in electronics and modern computer automation, including computer graphics. Increasing interest in the STM/SPM technique also exists in industry, where individual fabrication steps can be controlled on the assembly line. Commercially available STM/SPM instruments are generally much less expensive than high-resolution electron microscopes. These and other reasons might be given to explain the fact that ten years after the invention of the STM, several thousand instruments already exist world-wide and are being built. The still increasing interest in the STM/SPM technique is reflected in the statistics of the series of international STM conferences which started in 1985 (Fig. 0.3). Perhaps we should not

forget to mention an additional important (non-scientific?) reason why STM/SPM has attracted such a large number of scientists: the fascination of real-space images of atomic structures, sometimes exhibiting all the beauty that nature can offer to us on that scale . . .